

03070 VAT

**Hydroxy-functional binder components**Field of the Invention

The invention relates to hydroxy-functional binder components. It also relates to a process for the preparation of these binder components and to the binders prepared therewith and their use, in particular for formulation of glazes for wood and wood materials.

Background of the Invention

It has been known to prepare adducts by reaction of maleic anhydride with water-insoluble resins and oils which contain olefinic double bonds in a preferably isolated, that is to say non-conjugated, arrangement, the acid anhydride function being retained. By reaction with hydroxy-functional products, these adducts can give half-esters, with ring opening and formation of one acid group per molecule of maleic anhydride added. These carboxy-functional half-esters can be emulsified in water after at least partial neutralisation of the acid groups; binders can be formulated with these emulsions. However, the storage stability and the drying properties of paints, impregnating agents and glazes for wood and wood materials based on these binders are unsatisfactory. For this reason, these emulsions are not used as the sole binder in combination with suitable curing agents, but must be mixed with other water-dilutable binders.

Such mixtures, however, have an inadequate storage stability. There is a need, therefore, to create products from the adducts mentioned that can be formulated by reaction with suitable reaction partners to sole binders for storage-stable and fast-drying paints and glazes. In this context, hydroxyl groups are preferred as the functional groups.

### Summary of the Invention

The invention therefore relates to hydroxy-functional binder components **ABC** obtainable by reaction of olefinically unsaturated compounds **A** having at least one  
5 olefinic double bond and a molar mass of from 400 g/mol to 6,000 g/mol, preferably from 500 g/mol to 5,000 g/mol, selected from the group consisting of oils, partly saponified or partly transesterified oil, alkyd resins of low molar mass, and oligomers or polymers of diolefins,  
10 olefinically unsaturated cyclic acid anhydrides **B**, and hydroxyamines **C** having at least one primary amino group and at least one hydroxyl group, wherein the radicals of the acid anhydrides **B** are bonded to the compounds **A** by a carbon-carbon bond, and wherein the acid anhydride groups  
15 are converted into acid imide groups by reaction with the hydroxyamines **C**. The reaction products **ABC** therefore contain a linear or branched main chain which has a polymethylene structure  $-(CH_2)_n-$  or a polyester structure or a structure derived from fatty acid esters of glycerol  
20 or other polyhydric alcohols, and, grafted onto this, cyclic imide structures, the imide nitrogen atom being substituted by a hydroxyalkyl group or a hydroxyalkyl-aryl group.

### Detailed Description of the Preferred Embodiments

25 The olefinically unsaturated compounds **A** contain at least one, preferably two or more olefinic double bonds, the olefinic double bonds preferably being in isolated, in particular non-conjugated arrangement. They are preferably selected from the group consisting of oils,  
30 partially saponified oils or partially transesterified oils, these oils having an iodine number of preferably from 100 cg/g to 220 cg/g, particularly preferably from 120 cg/g to 210 cg/g. "Partially saponified" is understood here as meaning oils which contain at least  
35 one free hydroxyl group by saponification. "Partially transesterified" is understood as meaning oils which

contain free hydroxyl groups by reaction with di- or polyhydric alcohols under transesterification conditions.

Suitable olefinically unsaturated cyclic acid anhydrides **B** are intramolecular anhydrides of aliphatic and cycloaliphatic dicarboxylic acids having from 4 to 16 carbon atoms and at least one olefinic double bond, in particular maleic anhydride and tetrahydrophthalic anhydride.

Suitable hydroxyamines **C** are aliphatic linear, branched or cyclic hydroxyamines having at least one hydroxyl group and at least one primary amino group and at least two carbon atoms. Suitable compounds are, for example, ethanolamine, 3-aminopropanol, 3- and 4-aminobutanol, 5-aminopentanol, 6-aminohexanol, 4-hydroxycyclohexylamine, 1-amino-4-(2-hydroxyethyl)piperazine, aromatic-aliphatic hydroxyamines, in which at least one amino group is bonded to an aromatic or aliphatic carbon atom and at least one hydroxyl group is bonded to an aliphatic carbon atom, such as o- and m-aminobenzyl alcohol, and dihydroxyalkylamines, such as N,N-bis(2-hydroxyethyl)-ethylenediamine.

Adducts **ABC** which are particularly preferred are reaction products of oils, in particular linseed oil, soy bean oil and tall oil, alkyd resins of low molar mass derived from oils and fatty oils by transesterification with polyhydric alcohols, such as glycerol, trimethylolpropane and pentaerythritol or with polybasic acids or anhydrides thereof, such as phthalic acid (anhydride), and homopolymers of butadiene or isoprene or copolymers thereof with ethylene, propylene or 1-butene, with maleic anhydride or tetrahydrophthalic anhydride or mixtures thereof, and ethanolamine.

The adducts **ABC** containing hydroxyl groups can be reacted by a large number of further reactions to give binders for coating compositions. In this context, the hydroxyl

groups are reacted either with low molar mass or high molar mass compounds **D'** containing acid groups in an esterification reaction or with low molar mass compounds **D''** containing isocyanate groups in an addition reaction.

- 5 Suitable reaction partners **D'** containing acid groups are selected from the group consisting of polybasic acids **D1** having at least two acid groups, fatty acids **D2** grafted with olefinically unsaturated acids, oils **D3** grafted with olefinically unsaturated acids, and polymers **D4**,  
 10 containing acid groups, of olefinically unsaturated monomers.

- Suitable reaction partners **D''** containing isocyanate groups are chosen from reaction products **D5** of polyfunctional isocyanates with compounds which contain  
 15 at least one group which is reactive towards isocyanates and at least one acid group, and adducts **D6** of polyfunctional isocyanates with olefinically unsaturated compounds containing hydroxyl groups.

- Suitable polybasic acids **D1** are aliphatic or aromatic  
 20 compounds having at least one carboxyl group and at least one further acid group chosen from carboxyl groups, sulfur-containing acid groups, in particular sulfonic acid groups  $-\text{SO}_3\text{H}$  and sulfinic acid groups  $-\text{SO}_2\text{H}$ , and phosphorus-containing acid groups chosen from phosphonic acid groups  $-\text{PO}_3\text{H}_2$ , phosphonous acid groups  $-\text{PO}_2\text{H}_2$  and  
 25 phosphinic acid groups  $-\text{POH}_2$ . It is also possible to use, instead of the free acids, their anhydrides. Trimellitic acid and its anhydride as well as sulfoisophthalic acid are particularly suitable.

- 30 Suitable grafted fatty acids **D2** are obtained from fatty acids **D21** having from 12 to 30 carbon atoms, which contain at least one olefinic double bond, and olefinically unsaturated acids **D22** having from 3 to 8 carbon atoms, which contain at least one carboxyl group  
 35 and at least one olefinic double bond. Suitable fatty

acids **D21** are linoleic acid, linolenic acid, oleic acid and palmitoleic acid. Suitable low molar mass unsaturated acids are acrylic acid, methacrylic acid, vinylacetic acid, maleic acid, tetrahydrophthalic acid and itaconic acid. In the grafting reaction, further olefinically unsaturated copolymerisable monomers **D23** may also be used, in a mixture with the said acids **D22**, such as, for example, styrene, p-methylstyrene, methyl (meth)acrylate, ethyl (meth)acrylate, isobutyl (meth)acrylate and 2-ethylhexyl (meth)acrylate.

Suitable grafted oils **D3** are such oils **D31** which are grafted with acids **D22** and optionally, the further monomers **D23**, which oils **D31** contain at least one olefinic double bond in the molecule. Suitable oils **D31** are, in particular, wood oil, soya oil and linseed oil having iodine numbers of from 100 cg/g to 220 cg/g, preferably of from 120 cg/g to 210 cg/g.

Suitable acid copolymers **D4** are copolymers of acids **D22**, in particular of acrylic and methacrylic acid, with copolymerisable monomers selected from the group consisting of alkyl esters of acids **D22**, in particular methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, the isomeric butyl (meth)acrylates and 2-ethylhexyl (meth)acrylate, hydroxyalkyl esters of acids **D22**, in particular hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate and hydroxybutyl (meth)acrylate, styrene, vinyltoluene, and p-methylstyrene. Copolymers of (meth)acrylic acid, methyl (meth)acrylate, (iso-)butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, hydroxyethyl (meth)acrylate and (p-methyl-)styrene are particularly preferred.

Suitable adducts **D5** of isocyanates with compounds which contain an acid function and at least one group which is reactive towards isocyanates are hydroxy acids **D51** as well as amino acids **D52** and mercapto acids **D53** with at least difunctional isocyanates **D54**, in particular

diisocyanates, which are aromatic or aliphatic and are chosen, in particular, from toluylene-diisocyanate, tetramethylxylylene-diisocyanate, bis(4-isocyanatophenyl)methane, hexamethylene-diisocyanate, 5 isophorone-diisocyanate, trimethylhexane-diisocyanate and the allophanates, isocyanurates, biurets and uretdiones derived from these isocyanates. The hydroxy, amino and mercapto acids preferably contain sterically hindered acid groups, that is to say those which do not react or 10 react only slowly with isocyanates under decomposition and evolution of carbon dioxide.

Suitable adducts **D6** are reaction products of polyfunctional isocyanates **D61** with olefinically unsaturated monomers which contain groups that are 15 reactive towards isocyanates, such as hydroxyl groups, mercaptan groups or amino groups. Suitable compounds are, in particular, hydroxyalkyl esters of the acids mentioned under **D22**, such as hydroxyethyl and hydroxypropyl (meth)acrylate.

20 The reaction with low molar mass acids **D'** is carried out under condensation conditions and with enlargement of the molecule, a polyester being formed from adducts **ABC** having at least two hydroxyl groups and low molar mass acids **D'** having likewise at least two acid groups. In 25 this context, the amounts of the educts **D'** and **ABC** are to be chosen so that an excess of acids **D'** is employed, as a result of which condensation products having an acid number of from approximately 10 mg/g to approximately 100 mg/g, preferably from 20 mg/g to 80 mg/g, are 30 prepared.

In the reaction of high molar mass compounds **D'** containing acid groups and having acid numbers of from 10 mg/g to 50 mg/g, only a low decrease in the acid number is observed during the condensation. Still, 35 whereas a sample of the still unreacted reaction mixture comprising the adduct **ABC** and the high molar mass

compound **D'** containing acid groups does not yield a homogeneous mixture on dilution in 10 times the mass of water, after condensation for approximately 8 hours, the reaction mixture becomes water-dilutable, and in the condensed reaction mixture diluted with water no phase separation is observed even after being left to stand for 24 hours at room temperature (23 °C).

By reaction with the compounds **D5** containing isocyanate groups and acid groups, products are formed which contain acid groups instead of the hydroxyl groups and which are suitable in particular as additives to other water-dilutable binders to increase the mass fraction of solids thereof. In the reaction with compounds **D5** that contain two isocyanate groups and one acid group, such as, for example, the reaction products of dimethylolpropionic acid or dimethylolacetic acid with preferably aliphatic diisocyanates or reaction products of monohydroxy acids with triisocyanates, such as the isocyanurates of the abovementioned diisocyanates, reaction products are obtained which contain two radicals of the adducts **ABC** and one acid group and which can already be employed as sole binders or as resin for admixing to other binders.

Finally, the reaction of the adducts **ABC** with the reaction products **D6** of diisocyanates and hydroxyalkyl esters of olefinically unsaturated acids leads to substances which can be employed as binders in radiation-curable coating compositions and which are distinguished by a low viscosity and high reactivity.

The invention is illustrated by the following examples.

### 30 Examples

#### **Example 1**      Resin 1 containing acid groups

700 g of tall oil fatty acid, 92 g of glycerol and 0.8 g of triphenyl phosphite were charged into a reactor and

heated to 230 °C. The water of reaction was distilled off azeotropically by addition of 25 g of xylene, and the xylene separated from the water was recycled.

5 Esterification was carried out at this temperature for approximately five hours with removal of water, until the acid number of the reaction mixture had fallen to less than 2 mg/g.

10 After addition of 30 g of phthalic anhydride, esterification was continued for three more hours to an acid number of less than 6 mg/g, with the water of reaction being separated. The xylene was then removed by distillation under reduced pressure.

A liquid resin having the following data was obtained:

15 mass fraction of solids: 99.2 %  
acid number: 4.7 mg/g  
dynamic viscosity (23 °C, 100 s<sup>-1</sup>): 128 mPa·s

#### **Example 2** Oil grafted with maleic acid

500 g of soybean oil and 100 g of maleic anhydride were charged into a reactor and the reactor was freed from  
20 atmospheric oxygen by successive cycles of evacuation and filling with inert gas. The mixture was heated up to 140 °C under an inert gas blanket and the temperature was then increased to 210 °C in the course of two further hours. The reaction mixture was kept at this temperature  
25 for approximately three hours until the adduct formation was concluded. Free maleic anhydride could no longer be detected. A liquid resin having the following data was obtained:

30 mass fraction of solids: 99.1 %  
Acid number: 92.2 mg/g (determined as the half-ester)  
Dynamic viscosity (23 °C, 25 s<sup>-1</sup>): 4,750 mPa·s



**Example 3** Fatty acid grafted with (acid) vinyl monomers

71 g of linseed oil fatty acid were introduced into a reactor and heated to 140 °C. A mixture comprising the monomers isobutyl methacrylate (55 g), p-methylstyrene (10 g) and methacrylic acid (35 g) was uniformly added dropwise in the course of approximately 7.5 hours, and at the same time 4 g of di-tert.-butyl peroxide were added. When the addition had ended, the reaction mixture was stirred further at 140 °C until a conversion of more than 95 % resulted from the mass fraction of solids measured. In a repeat experiment, it was possible to accelerate the reaction by addition of further peroxide. By applying a reduced pressure (approximately 100 hPa = 100 mbar) at the reaction temperature, it was possible to virtually quantitatively remove the residual monomers in the course of approximately 20 minutes. The cooled reaction mixture was diluted with xylene. A resin solution with the following data resulted:

mass fraction of solids:	85 %
Acid number:	200 mg/g

**Example 4** Adduct from Example 2 reacted with hydroxyamine

600 g of the resin from Example 2 and 165 g of xylene were charged into a reactor. 61 g of ethanolamine were added in the course of ten minutes under stirring, and the temperature rose to approximately 85 °C due to the exothermic reaction. After the exothermicity had subsided, the mixture was heated further to 160 °C, and the water of reaction was removed by azeotropic distillation with the xylene, phase separation and recycling of the xylene. The mixture was kept at 160 °C for three further hours until an acid number of less than 10 mg/g was measured on a sample taken from the reaction mixture. The xylene which remained was removed by

distillation under reduced pressure. A resin having the following data resulted:

mass fraction of solids: 99.4 %  
Acid number: 7 mg/g

- 5 **Example 5** Condensation product of the adduct ABC of Example 4 with a grafted fatty acid of Example 3

643 g of the resin from Example 4 and 588 g of the resin from Example 3 were introduced into a reactor and heated to 190 °C. The water of reaction formed during the esterification was distilled off azeotropically together with the xylene of the resin solution of Example 3; the xylene separated was recycled into the reaction mixture. The condensation was continued for approximately two hours until a Staudinger index of 7 cm<sup>3</sup>/g was determined on a sample taken. The xylene which remained was subsequently distilled off under reduced pressure. A resin having the following data resulted:

mass fraction of solids: 99.3 %  
20 Acid number: 62.5 mg/g  
Staudinger index 7.5 cm<sup>3</sup>/g

The reactor was then cooled and the contents were emulsified starting at a temperature of 95 °C by addition of aqueous ammonia solution (25 g of NH<sub>3</sub> in 100 g of the solution) and of 1,640 g of distilled water, under stirring. The following values were determined on the emulsion obtained:

mass fraction of solids: 40 %  
Acid number: 68 mg/g  
30 pH\* 8.15  
Dynamic viscosity (23 °C, 10 s<sup>-1</sup>): 10 Pa·s  
Average particle size 36.5 nm

\* Measurement after dilution to a mass fraction of solids of 10 % in aqueous solution

Using this emulsion, a clear coat paint was formulated which, when brushed onto wood, yielded a glossy coating with good wood wetting.

**Example 6**      Condensation product of the resin of  
Example 4 with a low molar mass acid

643 g of the resin from Example 4 and 135 g of trimellitic anhydride were charged into a reactor and heated to 160 °C. By addition of the anhydride and partial esterification, the Staudinger index (measured in chloroform at 23 °C) of samples taken rose to 8.5 cm<sup>3</sup>/g in the course of two and a half hours. When this value was reached, the mixture was cooled and emulsified by addition of a mixture of 58 g of an aqueous ammonia solution (25 g of NH<sub>3</sub> in 100 g of the solution) and 1,310 g of distilled water, while stirring. The following values were determined on this resin emulsion:

mass fraction of solids:	36 %
Acid number:	88 mg/g
pH*	8.25
Dynamic viscosity (23 °C, 10 s <sup>-1</sup> ):	7.55 mPa·s
Average particle size	67 nm
* Measurement as above	

Using this emulsion, a clear coat paint could be formulated which, when brushed on to wood, gave a glossy coating with good wood wetting.

~  
o-o-o-o